Sources of Polarizability

The net polarizability of a dielectric material results mainly from the following 3 types of contributions:

(i) Electronic polarizability
(ii) Ionic polarizability
(iii) Dipolar or Orientational polarizability

The extent to which a particular polarizability contributes depends on the nature of the dielectric and the frequency of the applied electric field.

Electronic Polarizability

When an electric field is applied to the dielectric, the positively charged nucleus and electrons of an atom are displaced in opposite directions and electronic polarization occurs. The electron cloud shifts towards the +ve end of the field as shown in fig(B). Dipole moment is created in each atom due to the relative shift of the centre of the electron cloud and the nucleus. The shift is proportional to the applied electric field $\vec{E}$ and the induced dipole moment of the atom:

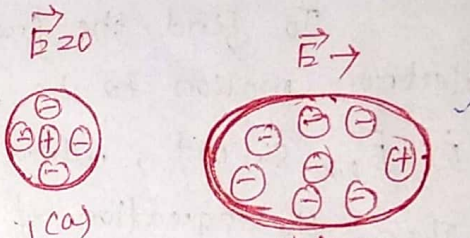

Fig.

$$\vec{P}_e = \alpha_e \vec{E}$$

where, α_e = electronic polarizability which is independent of temp. of the dielectric.

Classical theory of Electronic Polarizability

Let ω_0 be the natural frequency of vibration of an electron bound harmonically to the atom, then it exhibits resonant absorption at frequency ω_0 and is given by,

$$\omega_0 = \sqrt{\beta/m} \quad \text{---- (1)}$$

where ω

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where, β = force-const.
and m = mass of the electron.

Under equilibrium condition, the force on the electron due to local field ($-e\vec{E}_{loc}$) is equal to the force of restitution (βx), where x is the displacement of the electron from the mean position i.e.,

$$-e\vec{E}_{loc} = \beta x = m\omega_0^2 x \quad \text{---(2)}$$

The static electronic polarizability is given by,

$$\alpha_e = \frac{P}{E_{loc}} = \frac{-ex}{\left(\frac{m\omega_0^2 x}{-e}\right)} = \frac{e^2}{m\omega_0^2} \quad \text{---(3)}$$

To find the frequency dependence of α_e we assume the electron motion to be simple harmonic and the local field $\vec{E} = \vec{E}_{loc} \sin\omega t$, where ω is the frequency of the field $\vec{E}$. Then the equation of motion of the electron is,

$$m\frac{d^2x}{dt^2} + m\omega_0^2 x = -eE_{loc}\sin\omega t \quad \text{---(4)}$$

Substituting $x = x_0 \sin\omega t$.

$$m\frac{d^2}{dt^2}(x_0 \sin\omega t) + m\omega_0^2 x_0 \sin\omega t = -eE_{loc}\sin\omega t$$

$$\Rightarrow m(\omega_0^2 - \omega^2)x_0 = -eE_{loc} \quad \text{---(5)}$$

The amplitude of the dipole oscillation is,

$$P_0 = -ex_0 = \frac{e^2 E_{loc}}{m(\omega_0^2 - \omega^2)} \quad \text{---(6)}$$

∴ The frequency dependent electronic polarizability is given by,

$$\alpha_e = \frac{P_0}{E_{loc}} = \frac{e^2/m}{(\omega_0^2 - \omega^2)} \quad \text{---(7)}$$

The corresponding quantum mechanical expression is,

$$\alpha_e = \frac{e^2}{m}\sum \frac{f_{ij}}{\omega_{ij}^2 - \omega^2} \quad \text{---(8)}$$

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f_{ij} is the oscillator strength of the electronic dipole transition b/w the atomic states i and j. α_e is independent of temperature.

If N be the no. of atoms per unit vol. of the dielectric then electronic static polarization is,

$$P_e = N P_e = N\alpha_e E_{loc} \quad \text{——— (9)}$$

And also we know that,

$$P_e = D - \varepsilon_0 E_{loc} \quad (\because \vec{D} = \vec{P} + \varepsilon_0 \vec{E})$$

$$\Rightarrow P_e = \varepsilon_0 \varepsilon_r E_{loc} - \varepsilon_0 E_{loc}$$

$$\Rightarrow P_e = \varepsilon_0 (\varepsilon_r - 1) E_{loc}$$

$$\therefore \varepsilon_0 (\varepsilon_r - 1) E_{loc} = N\alpha_e E_{loc}$$

$$\Rightarrow \boxed{\alpha_e = \frac{\varepsilon_0 (\varepsilon_r - 1)}{N}}$$

Dipolar or Oriental Polarizability

The molecules like H_2O, CH_3Cl, etc. having a permanent dipole moment are called dipolar or polar molecules. The substance comprising of such molecules is called dipolar substance.

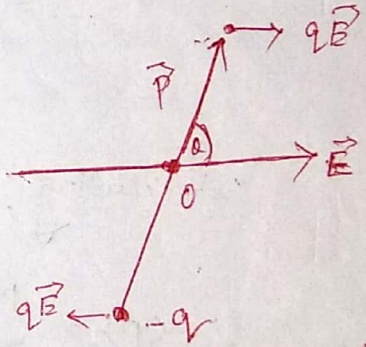

Fig:- A dipole moment $\vec{P}$ in an electric field $\vec{E}$.

In absence of external electric field $\vec{E}$ the dipoles are randomly oriented and the net dipole moment of the substance is zero. But in presence of an external electric field $\vec{E}$ the dipoles orient along $\vec{E}$ producing oriental polarizability. The thermal agitation of the molecules tends to disorient the dipoles and in equilibrium condition the different dipoles are oriented at various angles $\theta = 0$ to π radian with the direction of the external field ($\vec{E}$).

The PE of such a dipole oriented at an angle θ with $\vec{E}$ as shown in fig is given by,

$$U = -\vec{P} \cdot \vec{E} = -PE\cos\theta \quad \text{— (1)}$$

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The no. of dipoles oriented b/w θ and $d\theta$ i.e. within solid angle $d\Omega = 2\pi \sin\theta d\theta$ is proportional to,

$$e^{(-U/kT)} d\Omega \text{ or } e^{\left(\frac{pE\cos\theta}{kT}\right)} 2\pi \sin\theta d\theta \quad \text{---(2)}$$

where, k = Boltzmann const. and T = absolute temp. of the material.

The contribution of the above no. of dipoles to the total polarization is, $2\pi p\, e^{(pE\cos\theta/kT)} \cos\theta \sin\theta d\theta$ —(3)

If there are N no. of dipoles in the material, then the average contribution to polarization is,

$$\langle p \rangle = \frac{\text{Total polarization due to } N \text{ dipoles}}{\text{Total no. of dipoles } (N)}$$

$$= p \frac{2\pi \int_0^{\pi} e^{(pE\cos\theta/kT)} \cos\theta \sin\theta d\theta}{2\pi \int_0^{\pi} e^{(pE\cos\theta/kT)} \sin\theta d\theta}$$

Substituting, $pE/kT = x$ and $\cos\theta = y \Rightarrow dy = -\sin\theta d\theta$

$$\therefore \langle p \rangle = \frac{p \int_{+1}^{-1} y e^{xy} dy}{\int_1^{-1} e^{xy} dy}$$

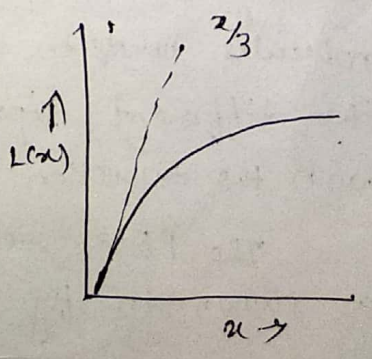
$$\Rightarrow \frac{\langle p \rangle}{p} = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \left(\coth x - \frac{1}{x}\right) \quad \text{---(4)}$$

$$\Rightarrow \frac{\langle p \rangle}{p} = L(x); \text{ where } L(x) = \coth x - 1/x = \text{Langevin's function.}$$

(5)

From the variation of $L(x)$ with x, we have for $x \ll 1$ or $pE \ll kT$,

$$L(x) = \frac{x}{3} = \frac{pE}{3kT} \quad \text{---(6)}$$



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Then from eq^n (5),

$$\langle p \rangle = p\left(\frac{pE}{3KT}\right) = \frac{p^2 E}{3KT}$$

The dipolar polarization is,

$$P = N\langle p \rangle = \frac{N p^2 E}{3KT}$$

∴ the dipolar (or oriental) polarizability is,

$$\alpha_d = \frac{\langle p \rangle}{E} = \frac{p^2}{3KT}$$

Thus the dipolar polarizability is inversely proportional to the absolute temp. of the dielectric.

* resonant absorption :- absorption of energy at natural frequency by a material.

* Ionic polarization :- Ionic polarization occurs only in those dielectric materials which possess ionic bonds such as NaCl. When such a material is subjected to an external field, the cations and anions get displaced in opposite direction, which gives rise to a net dipole moment.

$$P_i = n\alpha_i \vec{E}$$

↳ ionic polarizability

* Dipolar / orientational polarization :- Polar dielectrics exhibits orientational polarizability. Even in the absence of external electric field the polar dielectrics exhibits dipole moment. The orientations of molecules are random and hence net dipolemoment is zero. When an external $\vec{E}$ is applied these dipoles align in the direction of the applied $\vec{E}$. This type polarization is known as dipolar polarization.

dipolar polarizability, $\alpha_0 = p^2/3KT$

$$P_0 = \frac{n p^2 E}{3KT}$$

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POLARIZABILITY

When a dielectric is placed in a DC electric field ($\vec{E}$), it gets polarized by the following four processes:

(i) Electronic polarization

(ii) Ionic polarization (iii) Dipolar polarization

(iv) Space-charge polarization.

The contribution of a particular process depends on the nature of the dielectric as well as on the frequency of the applied electric field provided the applied field be an AC field.

Ionic Polarization / Ionic polarizability

The ionic polarizability arises due to the displacement of a charged ion (i.e cations and anions) in opposite directions in an ionic solid.

Let an electric field be applied along the positive directions when the positive ions when the positive ion moves towards by x_1 and the negative ion by $-x_2$. If each unit cell of the dielectric contains one +ve & one -ve ions, then the dipole moment due to ionic displacement is $\vec{p} = e(\vec{x_1} + \vec{x_2})$ —— (1)

If $\vec{F}$ be the force due to applied field $\vec{E}$ and β_1 and β_2 the force constants of cation and anion, then

$$\vec{F} = \beta_1 \vec{x_1} = \beta_2 \vec{x_2}$$

$$\therefore \vec{x_1} = \frac{\vec{F}}{\beta_1} = \frac{e\vec{E}}{m\omega_0^2}$$

where, $\vec{F} = e\vec{E}$ and the restoring force const. $\beta_1 = m\omega_0^2$

Similarly, $\vec{x_2} = \frac{e\vec{E}}{M\omega_0^2}$; m and M are the masses of the anion and cation respectively.

$$\therefore \vec{x_1} + \vec{x_2} = \frac{e\vec{E}}{\omega_0^2}\left(\frac{1}{M} + \frac{1}{m}\right)$$

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$$\Rightarrow \vec{P} = e(x_1 + x_2) = \frac{e^2 \vec{E}}{\omega_0^2}\left(\frac{1}{M} + \frac{1}{m}\right)$$

∴ ionic polarizability,

$$\alpha_i = \frac{\vec{P}}{\vec{E}} = \frac{e^2}{\omega_0^2}\left(\frac{1}{M} + \frac{1}{m}\right)$$

$$\text{or, } \alpha_i = \frac{e^2}{\omega_0^2 \mu} = \frac{e^2}{\beta}$$

where $\beta = \omega_0^2 \mu$ and $\mu = \left(\frac{1}{M} + \frac{1}{m}\right)^{-1}$ = reduced mass of the anion and cation.

Thus α_i is inversely proportional to the square of the natural frequency (ω_0) of the molecule and it's reduced mass is μ.

Dipolar polarizability

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